

Synthesis and Characterization Studies of N₂O₂ (azo-azo methane) Ligand with Divalent Metal Ions (Co, Ni and Cu) complexes

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ABSTRACT

Neutral tetra dentate N₂O₂ type complexes of Co(II), Ni(II), and Cu(II) have been prepared using anew Schiff base formed by the condensation of 4-amino antipyrine with 3-[p-(2-pyrimidyl sulphamyl) phenyl azo] 2,4-pentanedione in alcohol medium. The ligand and its complexes were characterized on the basic of their micro analytical data, molar conductance, magnetic susceptibility, FTIR, Uv-Vis, and ¹HNMR. The data show that the complexes have the composition of [ML]X₂ type. The Uv-Vis and magnetic susceptibility data of the complexes suggest a square planar geometry a round the central metal ion.

Keywords: Azo- Azometine, complexation, transition metal ion.

1. INTRODUCTION

β-Diketimines, versatile ligand systems, have been long known to form complexes with almost every metal ion and metalloid. From the past five decades, the chelating behavior of β-diketones in metal chelates give more information a bout the structural and spectral properties¹⁻⁴. The of the active methylene group of the β-diketone with an amine group gives azo compound which can effectively react with amines to form Schiff bases⁵.

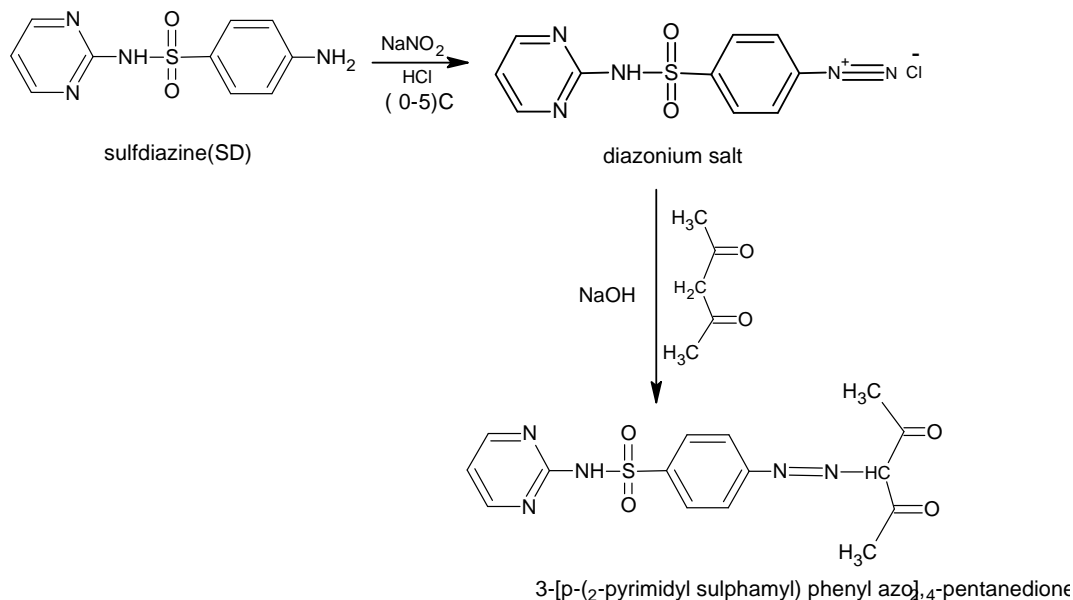
The chemistry of pyrazolone derivatives has attracted much attention because of their interesting structural properties and application in diverse areas⁶⁻⁸. The coordinating properly of 4-amino antipyrine has been modified into aflexible ligand system by condensation it with β-diketones and amines^{9,10}.

Schiff base and their transition metal complexes containing nitrogen oxygen donor atoms play an important role in biological and inorganic research and have been studied extensively due to their unique

coordination and biological properties¹¹. Schiff base complexes are involved in specific activities of pharmacology and physiology. They have wide application in various fields such as illness treatment, biochemical reaction and as biological regulators². In this paper we describe the

synthesis of ligand and its complexes.

Further insight into the bonding and possible geometrical structure has been made by micro analytical, FTIR, UV-Vis and spectral studies as well as magnetic and conductivity data.



Scheme.1: Preparation of the ligand (3-PSPA)

2. EXPERIMENTAL

2.1. Materials and measurements

All reagent and solvent were obtained from commercial sources were of highest purity and used as received. The electro thermal melting point moder 9300 was used to measure the melting point of the ligand and its complexes. Elemental analyses were carried out by means of micro analytical unit of 1180 C. H. N elemental analyzer. Electronic spectra (in ethanol)

were recorded on Shimadzu spectrophotometer double beam model 1700. UV-Vis spectrophotometer FTIR spectra were recorded in KBr medium on FTIR Shimadzu spectrophotometer model 8400 in wave number 4000-400 cm^{-1} . The ^1H NMR spectra were obtained in DMSO solution using (Bruker, Ultra Shield 3000 MKZ, Switzerland). Magnetic susceptibility measurements were carried out on a balance magnetic MSB-MKI using faraday method. The diamagnetic corrections were made by Pascal's constants¹².

2.2. Preparation of Schiff base ligand (3-PSPAP)

The ligand prepared as follows:

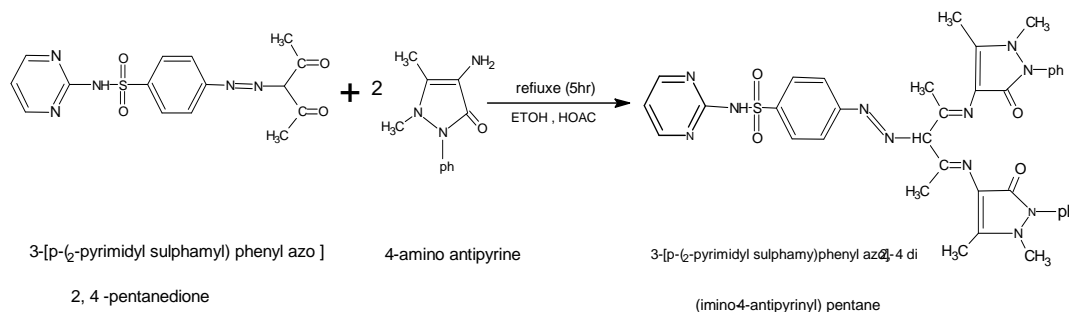
1. Preparation of the diazo dye

The heterocyclic azo ligand is prepared by coupling reaction of diazonium salt solution of sulphadiazine (SD) with appropriate amount of acetyl acetone as coupling component in alkaline solution. Diazonium solution is prepared by dissolving (2.50 g, 0.01 mol) of sulphadiazine in 5ml of concentrated hydrochloric acid and 20ml of distilled water. To this mixture a solution of (0.75g, 0.01 mol) of sodium nitrate in 10 ml of distilled water was added dropwise at (0-5)C°, and left to stand 30 min. This

diazonium solution was added dropwise into (1g, 0.01mol) acetyl acetone dissolved in 150 ml of ethanol and 50ml of (2N) sodium hydroxide at (0-5) C°. The mixture was allowed to stand over night. The precipitate was filtered off, washed with distilled water, and recrystallized twice from hot ethanol and then dried in over at 60 C° for 24 hours. m.p (203-205)d Scheme. 1.

2. Preparation of the Schiff base ligand.

The New Schiff base ligand was prepared by condensation of (3-PSPA) and 4-amino antipyrine in equimolar (1:2) mole ratio, in absolute alcohol. Few drops of glacial acetic acid were added to the reaction mixture and refluxed for (5h). The product was recrystallized from ethanol and dried over anhydrous CaCl₂. Scheme 2.



Scheme.2: Preparation of the ligand (3-PSPAP)

2.3. Preparation of metal complexes

The metal complexes were prepared by the mixing of 50ml ethanolic solution of (CoCl₂.6H₂O, NiCl₂.6H₂O, and CuCl₂.2H₂O) with the 50ml of ethanolic solution of Schiff base in (1:1) (metal:ligand) ratio. The resulting mixture was refluxed for 1h. Colored product appeared on standing and

cooling the a above solution. The precipitated complexes were filtered, washed and recrystallized with ethanol several times and dried over anhydrous CaCl₂ in desiccators.

3. RESULTS AND DISCUSSION

The analytical data for the ligand and complexes together with some physical

properties are summarized in Table 1. The analytical data of the complexes correspond well with the general formula $[ML]X_2$ where $M = \text{Co(II)}$, Ni(II) , and Cu(II) , $L = (3\text{-PSPAP})$. The magnetic moment of all these complexes at room temperature are consistent with square-planar geometry around the central metal ion. These complexes showed higher conductance values ($72\text{-}78 \text{ ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$) indicating their electrolytic nature¹³. The proposed structures for the ligand and complexes are given in Fig. 4.

3.1. Microanalysis

The elemental analysis data the complexes as shown in table (1) exhibit the formation 1:1 $[M:L]$ ratio. It was found that the theoretical values are in a good agreement with the found data. The purity of the Schiff base ligand were tested by TLC technique and C, H and N elemental analyses.

3.2. IR spectra

In order to clarify the mode of bonding and the effect of the metal ion on the ligand, the IR spectra of the free ligand and the metal complexes were studied and assigned based on careful comparison of their spectra with that of the free ligand. Relevant IR bands for the ligand and metal complexes are presented in table 2.

The bands in the region 3246 cm^{-1} and 3360 cm^{-1} due to stretching mode of NH in the spectra of the ligand undergo some change in the spectra of the complexes. The spectrum of ligand show band at 1495 cm^{-1} due to $(\text{N}=\text{N})$ group which is remains in the same region in free ligand and in

complexation¹⁴. Strong bands in 1674 cm^{-1} and 1660 cm^{-1} region in the ligand were observed due to $\nu(\text{C}=\text{O})$ of the keto group in a pyrazolone ring^{15,16}.

In the complexes, this bands are shifted to lower frequency at 1651 cm^{-1} and 1608 cm^{-1} , indicating the coordination of carbonyl oxygen to the metal ion which is further supported by the formation of new bands in the regions $(420\text{-}510)\text{cm}^{-1}$ and $(410\text{-}460) \text{cm}^{-1}$ which are attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ bands respectively^{17,18}. The spectrum of free ligand exhibit band at 1585 cm^{-1} which is characteristic of the azomethine group $(\text{C}=\text{N})$. In IR spectra of complexes, this band shifted to lower frequency of 1562 cm^{-1} which indicates that the azomethine nitrogen one of the coordination atoms in the Schiff base^{19,20}. The ligand shows two bands and 1356 cm^{-1} and 1155 cm^{-1} which assigned to $\nu(\text{SO}_2)$ asymmetric and symmetric respectively^(21,22).

3.3. Electronic Spectra and magnetic moments

The electronic spectral data of the ligand and metal complexes in ethanol field around the metal ion has been deduced from the electronic spectra. The electronic absorption spectrum of the ligand shows two bands at 362nm (27624 cm^{-1}) and 300nm (33333 cm^{-1}) which assigned to $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ respectively.

1- Cobalt (II) Complex

The spectrum of the Co(II) complex shows three bands at, 355nm (28169 cm^{-1}), 365nm (27397 cm^{-1}) and 655nm (15267 cm^{-1}) there are assigned to charge transfer and $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ respectively²³. The magnetic moment value of this complex is $(3.43)\text{B.M.}$

Thus the square planar geometry has been suggested for this Co(II) complex²⁴.

2- Nickel (II) Complex

The electronic spectrum of Ni(II) complex shows three bands at 365nm (27397cm⁻¹), 404nm (24752cm⁻¹) and 697nm (14347cm⁻¹) these are assignable to charge transfer and ¹A₁g→¹A₂g and ¹A₁g→¹B₁g respectively²⁵. This complex is diamagnetic in nature. Therefore a square planar geometry has been suggested²⁶.

3- Copper (II) Complex

The electronic spectrum of the Cu(II) complex exhibit bands at 303nm (33003cm⁻¹), 337nm (29673cm⁻¹) and 543nm (18416cm⁻¹) which have been assigned to charge transfer and ²B₁g→²A₁g transitions respectively⁽²⁷⁾. The magnetic moment of the complex is (1.88 B.M). therefore a square-planar stereochemistry has been suggested²⁸.

The electronic spectra of the ligand and the copper(II) as shown in Fig.1.

3.4. ¹HNMR spectrum studies

The ¹HNMR Spectra of the ligand was recorded in DMSO-d₆. The ¹HNMR spectrum of the ligand shows the following signals : phenyl multiples at (7.3 -7.8) δ range, -N-CH₃ at 3.1 δ, -C-NH at 4.0 δ, =N-CH at 1.5 δ, =C-CH₃ at 2.4 δ, N=C-CH₃ at 1.94 δ, and CH of primidine at (6.9-8.4) δ range as shown in Fig(3).

3.5. Molar Conductance measurements

All chelate complexes prepared in the work showed conductivity values ranged between (72.98-78.27) S. mol⁻¹. Cm² in DMSO at room temperature these values indicating that conductive species exist²³. According to these results the structural formulas of these ligand and complexes may be preposed in Fig. 4.

Table.1: Physical data and analysis of ligand and its complexes

No.	Compound	Colour	M.P °C	Yield %	Formula	Found,(Calc.)%			
						C	H	N	M
1	L=(3- PSPAP)	Red	204 d	75	[C ₃₇ H ₃₇ N ₁₁ SO ₄]	60.52 (60.73)	4.89 (5.06)	20.98 (21.06)	----
2	[CoL] Cl ₂	Purple	154-156	60	[Co C ₃₇ H ₃₇ N ₁₁ SO ₄]Cl ₂	51.23 (51.57)	4.02 (4.29)	17.37 (17.88)	6.58 (6.84)
3	[NiL] Cl ₂	Green	146-144	72	[Ni C ₃₇ H ₃₇ N ₁₁ SO ₄]Cl ₂	51.34 (51.58)	4.13 (4.29)	17.44 (17.89)	6.92 (6.82)
4	[CuL] Cl ₂	Green	125-126	70	[Cu C ₃₇ H ₃₇ N ₁₁ SO ₄]Cl ₂	51.17 (51.29)	4.07 (4.27)	17.56 (17.79)	7.04 (7.33)

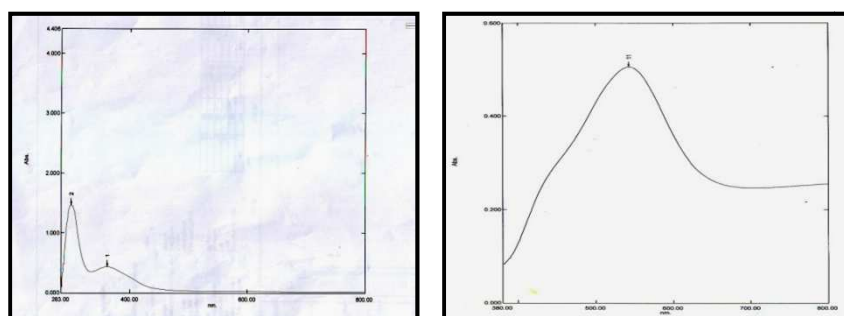
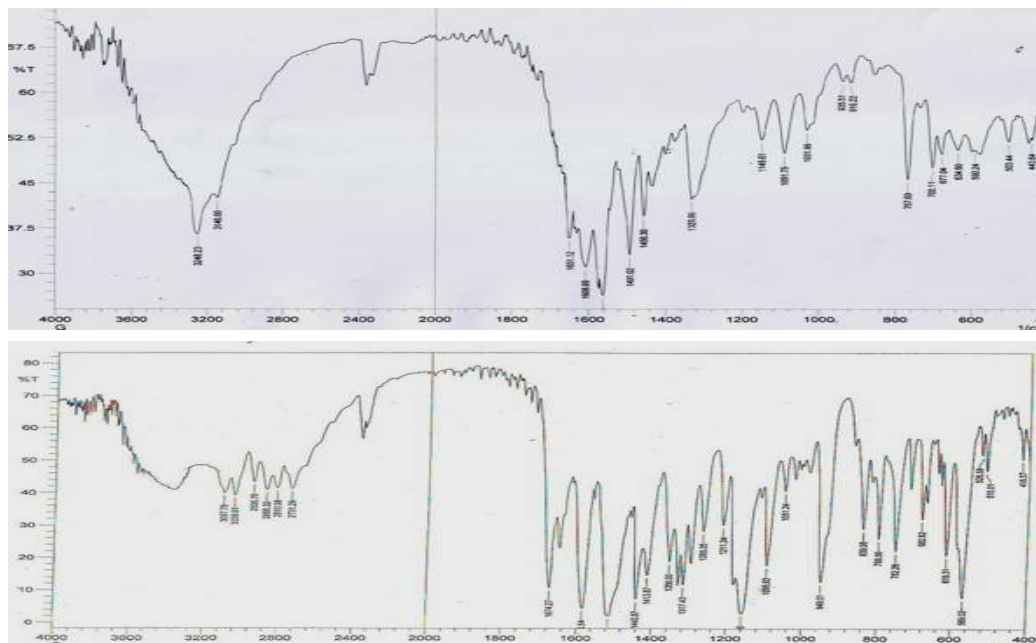
L =ligand, d =Complex metal with decomposition

Table.2: Some IR frequencies in (cm⁻¹) of the ligand and its metal complexes

Ligand/complexes	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{N=N})$	$\nu(\text{SO}_2)$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
L= (3- PSPAP)	1674 1660	1585	1495	1317 1150	---	---
[CoL] Cl ₂	1649 1614	1556	1499	1320 1148	510	440
[NiL] Cl ₂	1645 1612	1558	1496	1321 1146	507	443
[CuL] Cl ₂	1651 1608	1562	1491	1320 1149	503	445

Table.3 : Electronic spectra, conductivity and magnetic moment of complexes

Complexes	Abs. nm (cm ⁻¹)	Transition	Conductivity S.mol ⁻¹ . cm ²	μ_{eff} (B.M)
L=(3-PSPAP)	362nm (27624 cm ⁻¹) 300nm (33333 cm ⁻¹)	$\pi-\pi^*$ $n-\pi^*$	---	---
[CoL] Cl ₂	355nm (28169cm ⁻¹) 365nm (27397cm ⁻¹) 655nm(15267cm ⁻¹)	C.T C.T $^1A_{1g} \rightarrow ^1B_{1g}$	73.28	3.43
[NiL] Cl ₂	365nm (27397cm ⁻¹) 404nm (24752cm ⁻¹) 697nm (14347cm ⁻¹)	C.T $^1A_{1g} \rightarrow ^1A_{2g}$ $^1A_{1g} \rightarrow ^1B_{1g}$	72.98	Dia
[CuL] Cl ₂	303nm, (33003cm ⁻¹) 337nm, (29673cm ⁻¹) 543nm, (18416cm ⁻¹)	C.T C.T $^2B_{1g} \rightarrow ^2A_{1g}$	78.27	1.88

**Fig.(1). Electronic spectrum of : (a) the ligand (3-PSPAP)&(b) [CuL]Cl₂****Fig.(2): IR spectra of : (a) the ligand (3-PSPAP) & (b) [CuL]Cl₂**

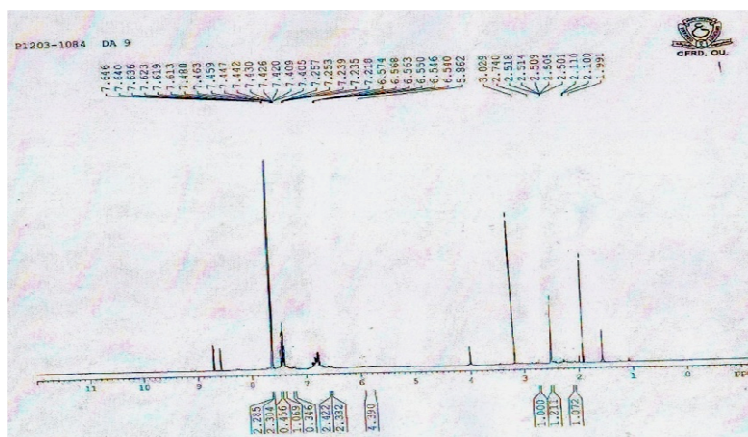
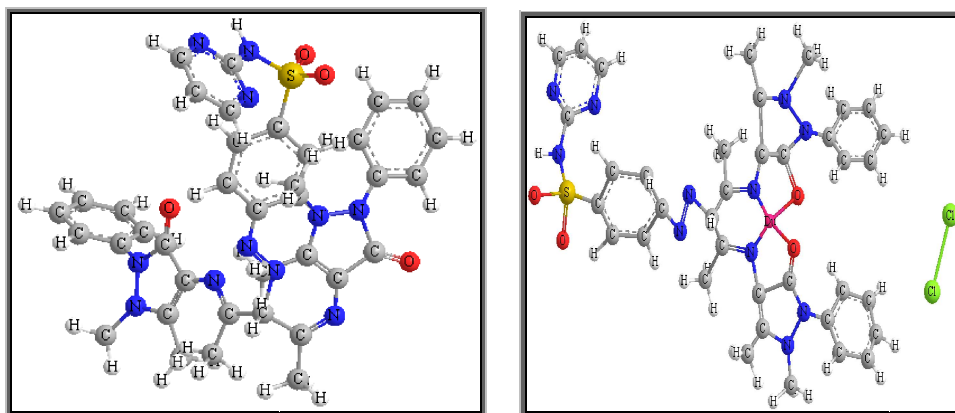
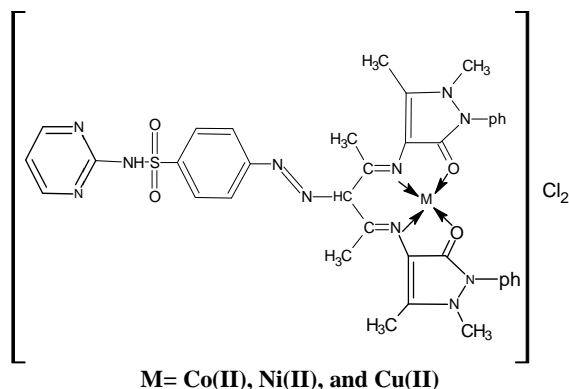
Fig.(3). ^1H NMR Spectrum of the ligand (3-PSPAP)

Fig. 4. Molecular structure of (a) 3-[p-(2-pyrimidyl sulphamy)phenyl azo]-2, 4 di (imino-4-antipyrinyl) pentane and (b) of the metal chelate complexes.



M= Co(II), Ni(II), and Cu(II)

Fig. 5: The proposed structural formula of the metal chelate complexes.

4. CONCLUSION

In the present work we have synthesized new ligand of Schiff base and its complexes, characterized by different analytical techniques and found that the complexes are inconsistent with our expected structures and revealed square planar geometry around metal ion, where the ligand act as tetradentate chelate with N_2O_2 donor sites forming five and six - member chelate rings.

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